# An ab Initio Study of the Kinetics of the Reactions of Halomethanes with the Hydroxyl Radical. 2. A Comparison between Theoretical and Experimental Values of the Kinetic Parameters for 12 Partially Halogenated Methanes

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Ab initio calculations have been performed for the H-atom abstraction reactions from a series of 12 halogenated methanes by the hydroxyl radical. Geometry optimization and vibrational frequency calculations were performed for reactants, transition states, and products at the MP2/6-311G(2d,2p) level of theory. Single-point energy calculations were carried out at the PMP4(SDTQ) level with both 6-311G(3df,2p) and 6-311++G(3df,3pd) basis sets. Canonical transition state theory with Wigner's tunneling correction was used to predict the rate constants as function of the temperature (250−400 K). It is found that the treatment of the kinetics of these reactions with the lower level of theory, PMP4(SDTQ)/6-311G(3df,2p)//MP2/6-311G(2d,2p), leads to results in good agreement with experimental values and suggests the possibility of using this methodology in the implementation of a theoretical tool that properly describes the kinetics of reactions such as hydrogen abstractions by OH radicals from partially halogenated organic compounds.

## Introduction

In the first paper of this series[1] (herein referred to as paper I), we initiated an investigation regarding the feasibility of applying relatively inexpensive ab initio electronic structure calculations together with canonical transition state theory, TST, leading to the generation of efficient and reliable computational tools that properly describe the kinetics of processes such as hydrogen-atom abstraction reactions by the hydroxyl radical from partially halogenated organic compounds. These reactions are of particular importance in the determination of the atmospheric lifetimes of compounds suggested as replacements for fully halogenated alkanes, widely used in industry. In light of the very large number of potential replacement compounds, and the need to select a few for more thorough evaluation, efficient computational screening methods are needed to help in establishing their environmental acceptability, along with other physical and chemical properties. Presently, there exists a wealth of reliable kinetic data on the reactions of OH with small haloalkanes.[2] These data can be very valuable in the validation of computationally efficient theoretical tools for predicting the reactivity of larger haloalkanes and as a starting point for calculations on halogenated compounds containing additional functional groups. In this work, we extend our previous study of the reaction of OH with $CH_2Br_2$ to the set of monohalomethanes ($CH_3F$, $CH_3Cl$, and $CH_3Br$), dihalomethanes ($CH_2F_2$, $CH_2FCl$, $CH_2Cl_2$, and $CH_2ClBr$), and trihalomethanes ($CHF_3$, $CHF_2Cl$, $CHF_2Br$, $CHFCl_2$, and $CHCl_3$). Although a few ab initio studies of the reactivity of OH toward some fluoro-chloro-substituted methanes have been previously performed at various levels of theory,[3−6] we decided also to include these reactions in our study in order to provide additional insight into the search for the minimum level of theory required for a reliable and efficient computational tool able to properly describe the kinetics of these and similar reactions.

In our investigation of the reaction of OH with $CH_2Br_2$, we demonstrated that full optimization of the geometric parameters for all stationary points at the second-order Møller−Plesset perturbation theory level, MP2, with the 6-311G(2d,2p) basis set was sufficient to provide reasonable values. Furthermore, in the calculation of the energetics of the reaction and the subsequent kinetic parameters, the best agreement with the experimental data was obtained by single-point calculations performed with the 6-311++G(3df,3pd) basis set employing unrestricted spin-projected second-order Møller−Plesset perturbation theory, PMP2/6-311++G(3df,3pd)//MP2/6-311G(2d,2p), and fourth-order Møller−Plesset perturbation theory, in the space of single, double, triple, and quadruple excitations, PMP4(SDTQ)/6-311++G(3df,3pd)//MP2/6-311G(2d,2p). In addition, a quite reasonable agreement for the value of the activation energy was obtained with the far less computationally intensive level of theory PMP4(SDTQ)/6-311G(3df,2p)//MP2/6-311G(2d,2p). Even though these results are encouraging, it is clear that a more extensive study including more reactions is needed in order to assess the possibility of computing the kinetic parameters for H-atom abstraction by OH radicals with this relatively inexpensive level of theory. In this study, we compare the use of both PMP4(SDTQ)/6-311G(3df,2p)//MP2/6-311G(2d,2p) and PMP4(SDTQ)/6-311++G(3df,3pd)//MP2/6-311G(2d,2p) levels of theory in the calculation of kinetic parameters for a set of mono-, di-, and tri-halomethanes, and the results are compared with the experimental kinetic data available in the literature.[2]

## Computational Methods[7]

All calculations described below were carried out with the Gaussian 94[8] suite of programs on a CRAYC90/6256 supercomputer and a 32-processor Silicon Graphics Origin 2000

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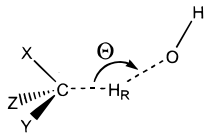
**TABLE 1: Essential Structural Parameters,[a] Imaginary Vibrational Frequencies for the Transition States of Each Reaction, and Internal Rotation Barrier of the −OH Group at the MP2/6-311G(2d,2p) Level of Theory**




| | $r$(C−H$_R$) | $r$(O−H$_R$) | Θ(OH$_R$C) | L[b] | $\nu^{\ddagger}$ (cm$^{-1}$) | $V_0$ (kJ mol$^{-1}$) | treatment of $\nu_{ROT}$(HO···H···C)[c] |
|---|---|---|---|---|---|---|---|
| $CH_3F$ | 1.194 | 1.303 | 162.5 | 0.315 | 2094i | 11.5 | harmonic |
| $CH_3Cl$ | 1.194 | 1.291 | 170.5 | 0.338 | 2182i | 6.9 | hindered rotor |
| $CH_3Br$ | 1.195 | 1.288 | 171.4 | 0.347 | 2194i | 6.7 | hindered rotor |
| $CH_2F_2$ | 1.195 | 1.294 | 164.6 | 0.329 | 2236i | 8.3 | hindered rotor |
| $CH_2FCl$ | 1.191 | 1.294 | 162.1 | 0.326 | 2203i | 8.5 | hindered rotor |
| $CH_2Cl_2$ | 1.188 | 1.294 | 168.0 | 0.326 | 2219i | 4.4 | hindered rotor |
| $CH_2ClBr$ | 1.188 | 1.294 | 167.9 | 0.326 | 2224i | 4.6 | hindered rotor |
| $CH_2Br_2$ | 1.188 | 1.296 | 165.3 | 0.324 | 2200i | 5.5 | hindered rotor |
| $CHF_3$ | 1.215 | 1.246 | 166.9 | 0.460 | 2560i | 4.9 | hindered rotor |
| $CHF_2Cl$ | 1.200 | 1.271 | 164.6 | 0.376 | 2376i | 6.6 | hindered rotor |
| $CHF_2Br$ | 1.195 | 1.281 | 162.8 | 0.352 | 2302i | 7.1 | hindered rotor |
| $CHFCl_2$ | 1.191 | 1.285 | 163.7 | 0.317 | 2262i | 7.3 | hindered rotor |
| $CHCl_3$ | 1.184 | 1.295 | 172.7 | 0.317 | 2236i | 2.6 | hindered rotor |

[a] Bond lengths $r$ are in angstroms, bond angles $\theta$ in degrees; the hydrogen atom involved in H-atom abstraction is noted H$_R$. [b] The parameter $L$ is the ratio between the elongation value of the C−H bond and the elongation value of the O−H bond in the transition state: $L = \delta r$(C−H)/$\delta r$(O−H). [c] Low-frequency mode associated with the −OH rotation around the axis along the C−H bond being broken.

parallel computer, as discussed in our previous publication.[1] Fully optimized geometries, harmonic frequencies, and zero-point energy corrections (ZPE) of reactants, transition structures, and products were calculated with the second-order Møller−Plesset perturbation theory (UMP2) using the 6-311G(2d,2p) basis set. Electron correlation was calculated with fourth-order Møller−Plesset perturbation theory in the space of single, double, triple, and quadruple excitations with full anihilation of spin contamination[9] as implemented in the Gaussian 94 package (noted in our results as PMP4). These single-point energy calculations were carried out with the 6-311G(3df,2p) and 6-311++G(3df,3pd) basis sets using geometries previously optimized at the MP2/6-311G(2d,2p) level. All relative energies quoted and discussed in this paper include zero-point energy corrections with unscaled frequencies obtained at the MP2/6-311G(2d,2p) level.

As in paper I,[1] canonical transition state theory[10] (TST) and tunneling corrections were used to predict the rate constants over the same range of temperatures as the experimental measurements (250−400 K). Accordingly, the rate constants, $k(T)$, were computed using the following expression:

$$k(T) = \Gamma(T)\frac{k_B T}{h}\frac{Q^{TS}(T)}{Q^{OH}(T)Q^{CHXYZ}(T)}\exp\left(-\frac{\Delta E}{k_B T}\right) \qquad (1)$$

where $Q^{OH}(T)$, $Q^{CHXYZ}(T)$, and $Q^{TS}(T)$, are the total partition functions for the hydroxyl radical, halomethane of type CHXYZ, and transition state respectively, at temperature $T$; $\Delta E$ is the activation energy including zero-point energy and thermal corrections to the internal energy; $k_B$ is Boltzman's constant, and $h$ is Planck's constant. The total partition function of all species can be cast in terms of the translational ($Q^X_T$), rotational ($Q^X_R$), electronic ($Q^X_e$), and vibrational ($Q^X_v$) partition functions. In computing the electronic partition function for the OH radical, $Q^{OH}_e$, the multiplicity of the states $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$, and the energy gap of 139.7 cm$^{-1}$ between the levels,[11] have been taken into consideration. $\Gamma(T)$ in eq 1 indicates the corresponding tunneling correction at temperature $T$. Given the demonstrated success of the Wigner's tunneling correction in the case of the reaction:

$$OH + CH_2Br_2 \rightarrow H_2O + CHBr_2 \qquad (R1)$$

we decided to adopt such methodology in the calculation of all tunneling corrections for the reactions reported in this work. As described in paper I,[1] the expression for Wigner's tunneling correction is given by

$$\Gamma(T) = 1 + \frac{1}{24}\left(\frac{h\nu^{\ddagger}}{k_B T}\right)^2 \qquad (2)$$

where $\nu^{\ddagger}$ is the imaginary frequency at the saddle point and the other terms have the same meaning as in eq 1. The rate constant calculations over the temperature range 250−400 K were carried out using the TURBO-RATE program.[12]

## Results and Discussion

**1. Geometry Parameters and Vibrational Frequencies.** Table 1 lists the essential structural parameters calculated at the UMP2/6-311G(2d,2p) level of theory for the transition states corresponding to the 12 reactions under study. All other structural parameters as well as those for halomethanes, and halomethyl radicals, are reported in the supplementary Tables 1S−8S of the Supporting Information. For the species containing fluorine atoms, the observed trends suggest that the transition state becomes increasingly product-like as the number of F atoms increases. These results are reflected by the systematic increase of the parameter $L$, which is defined as the ratio between the increase in length of the C−H bond being broken and the elongation of the O−H bond being formed, each with respect to its equilibrium value in the reactants and the products. This parameter characterizes the most important aspect of the geometric structure of the transition state. Values for this parameter are included in Table 1. By contrast, the opposite trend is observed in the case of Cl and Br substitution, where the $L$ parameter decreases with the degree of halogen substitution. For the 12 transition states, the eigenvector corresponding to the imaginary frequency was observed to be primarily a

**TABLE 2: Calculated Reaction Enthalpies $\Delta_r H$, $\Delta_r H$(ISO), and Vibrationally Adiabatic Barriers at PMP4(SDTQ)/6-311G(3df,2p)//MP2/6-311G(2d,2p) and PMP4(SDTQ)/6-311++G(3df,3pd)//MP2/6-311G(2d,2p) Levels of Theory**

| | | $\Delta_r H^{a,b}$ | $\Delta_r H(\mathrm{ISO})^{a,b}$ | vibrationally adiabatic barrier[a] |
|---|---|---|---|---|
| OH + $CH_3F$ | PMP4(SDTQ)/6-311G(3df,2p) | −64.8 | −75.8 | 16.1 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | −74.0 | −71.6 | 14.0 |
| | literature[c] | −75.2 | −75.2 | 12.5 |
| OH + $CH_3Cl$ | PMP4(SDTQ)/6-311G(3df,2p) | −69.5 | −80.5 | 14.7 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | −81.3 | −78.9 | 10.7 |
| | literature[c] | −81.5 | −81.5 | 11.6 |
| OH + $CH_3Br$ | PMP4(SDTQ)/6-311G(3df,2p) | −64.9 | −75.9 | 15.5 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | −76.3 | −73.9 | 12.0 |
| | literature[c] | −74.5 | −74.5 | 12.2 |
| OH + $CH_2F_2$ | PMP4(SDTQ)/6-311G(3df,2p) | −63.2 | −74.2 | 15.5 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | −70.4 | −68.0 | 14.9 |
| | literature[c] | −67.5 | −67.5 | 14.8 |
| OH + $CH_2FCl$ | PMP4(SDTQ)/6-311G(3df,2p) | −72.0 | −83.1 | 13.1 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | −80.7 | −78.3 | 11.0 |
| | literature[c] | −78.2 | −78.2 | 11.6 |
| OH + $CH_2Cl_2$ | PMP4(SDTQ)/6-311G(3df,2p) | −82.9 | −93.9 | 10.0 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | −92.5 | −90.1 | 6.7 |
| | literature[c] | −96.8 | −96.8 | 8.7 |
| OH + $CH_2ClBr$ | PMP4(SDTQ)/6-311G(3df,2p) | −81.0 | −92.0 | 10.3 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | −90.7 | −88.3 | 7.3 |
| | literature[c] | −89.3 | −89.3 | 7.7 |
| OH + $CH_2Br_2$ | PMP4(SDTQ)/6-311G(3df,2p) | −79.1 | −90.1 | 10.5 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | −88.7 | −86.3 | 7.9 |
| | literature[c] | −81.6 | −81.6 | 7.5 |
| OH + $CHF_3$ | PMP4(SDTQ)/6-311G(3df,2p) | −41.5 | −52.5 | 25.2 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | −48.7 | −46.3 | 24.3 |
| | literature[c] | −54.0 | −54.0 | 20.3 |
| OH + $CHF_2Cl$ | PMP4(SDTQ)/6-311G(3df,2p) | −61.0 | −72.0 | 16.2 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | −68.7 | −66.3 | 14.5 |
| | literature[c] | −76.6 | −76.6 | 13.3 |
| OH + $CHF_2Br$ | PMP4(SDTQ)/6-311G(3df,2p) | −66.0 | −76.9 | 13.9 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | −73.4 | −71.0 | 12.8 |
| | literature[c] | | | 11.6 |
| OH + $CHFCl_2$ | PMP4(SDTQ)/6-311G(3df,2p) | −77.3 | −88.3 | 10.1 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | −85.1 | −82.7 | 7.7 |
| | literature[c] | −85.3 | −85.3 | 10.4 |
| OH + $CHCl_3$ | PMP4(SDTQ)/6-311G(3df,2p) | −93.7 | −104.7 | 4.7 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | −101.0 | −98.7 | 1.9 |
| | literature[c] | −107.1 | −107.1 | 7.5 |

[a] Units are kJ.mol$^{-1}$. [b] Including the sum of thermal energies (ΔZPE + thermal energy corrections). [c] Literature values based on the $\Delta_f H°$ at 298 K for reactants and products taken from supplementary Table 9S of the Supporting Information. Experimental activation energies taken from ref 2, and ref 14 for the activation energy of the reaction OH + $CH_2ClBr$.

motion of the reactive hydrogen atom that is being transferred. The absolute values of the vibrational frequencies corresponding to these transition vectors are also reported in Table 1.

Direct inspection of the TS low-frequency modes (given in Table 8S of the Supporting Information) indicates that in all cases there are low-frequency modes consisting of an internal OH rotation about the nearly linear C−H−O axis. Given that, with the exception of the reaction of OH with $CH_3F$, the barriers for these rotations were sufficiently small (Table 1), these modes were treated as hindered rotors instead of a vibration. As explained in our first paper,[1] these modes were removed from the vibrational partition function for the TS, and the corresponding hindered rotor partition function $Q_{HR}(T)$ calculated by the method devised by Ayala and Schlegel[13] was included in the expression for the rate constant.[1] In the case of the reaction of OH with $CH_3F$, the rotational barrier was found to be large enough (11.5 kJ mol$^{-1}$ in Table 1) so the internal rotational mode was treated by the harmonic approximation.

**2. Reaction Enthalpies.** Table 2 summarizes the results for reaction enthalpies ($\Delta_r H$) at 298 K calculated directly using the difference between the electronic energy of products and reactants computed at the PMP4(SDTQ)/6-311G(3df,2p)//MP2/6-311G(2d,2p) and PMP4(SDTQ)/6-311++G(3df,3pd)//MP2/6-311G(2d,2p) levels of theory for the series of reactions OH + CHXYZ (X, Y, Z = H, F, Cl, or Br). With the exception of the reaction OH + $CHF_2Br$, the corresponding literature values are also listed for comparison purposes. Following a similar procedure to the one adopted in our earlier publication,[1] reaction enthalpies for the 12 reactions were also corrected by new values of $D_{298}$(H−CXYZ) computed at the both levels of theory proposed in this work, utilizing the following isodesmic reactions:

$$CH_3 + CHXYZ \rightarrow CH_4 + CXYZ \quad (X, Y, Z = H, F, Cl, \text{or Br}) \quad (R2)$$

The use of an isodesmic reaction, such as reaction R2, provides an indirect method that may lead to a more reliable value of the bond dissociation energy, mainly due to systematic cancellation of errors arising from insufficient treatment of electron correlation and incompleteness of the basis sets. In general, isodesmic reactions are characterized by having the same number and types of bonds on each side of the equation, so that the errors mentioned above are largely canceled when $D_{298}$(H−CHXYZ) is calculated. The reaction enthalpy for reaction R2 was computed at the same levels of theory as that for the abstraction reactions under study:

$$CHXYZ + OH \rightarrow CXYZ + HOH \qquad (X, Y, Z = H, F, Cl, \text{or } Br) \quad (R3)$$

Taking the experimental value of $D_{298}(H-CH_3) = 440$ kJ mol$^{-1}$,[15] we obtain calculated $D_{298}(H-CXYZ)$ values at the various levels of theory used in this work. These $D_{298}(H-CXYZ)$ quantities were then used in the calculation of the reaction enthalpy for reactions R3 by means of the following relation:

$$\Delta_r H(\text{ISO}) = D_{298}(H-CXYZ) - D_{298}(H-OH) \qquad (3)$$

Table 2 lists the different values of $\Delta_r H(\text{ISO})$ for all the reactions under study. In general, PMP4(SDTQ)/6-311G(3df,2p)//MP2/6-311G(2d,2p) underestimates the experimental values of the heats of reactions by up to 15 kJ mol$^{-1}$ when computed by direct subtraction of the energies between products and reactants. A better agreement is obtained at the PMP4(SDTQ)/6-311++G(3df,3pd)//MP2/6-311G(2d,2p) level of theory, where errors no larger than 7 kJ mol$^{-1}$ are observed. As observed in our previous work,[1] an excellent agreement with the results reported in the literature is obtained in the case of the heats of reactions computed using the isodesmic reactions shown in (R2).

The results of Table 2 indicate an increase in the endothermicity of the reaction with the progressive substitution of H atoms by fluorine while the substitution by chlorine atoms leads to increased exothermicities. These trends can be explained by the relatively large $\sigma$ acceptor and $\pi$ donor characters of fluorine when compared to chlorine and bromine. Thus, the interaction between two or more adjacent fluorine atoms stabilizes the fluoromethane, while similar interactions between chlorine atoms as well as between bromine atoms have a negligible stabilizing effect. In addition, geminal interactions between fluorine and second and/or third row halogen atoms (Cl and Br) on the same halomethane lead to a weak stabilization.[16]

**3. Reaction Barriers.** Table 2 shows the computed vibrationally adiabatic barriers, VAB, for the 12 reactions under study. The following relation defines these barriers:

$$\text{VAB} = E_{TS} - E_R + \text{ZPE}_{TS} - \text{ZPE}_R \qquad (4)$$

where $E_{TS}$ and $E_R$ are the ab initio energies of the transition state and reactants, while $\text{ZPE}_{TS}$ and $\text{ZPE}_R$ are their corresponding zero-point energy corrections. The experimental activation energies, $E_a$, as reported in the literature are also listed in Table 2 for comparison purposes. Overall, the agreement between the barriers computed at the PMP4(SDTQ)/6-311++G(3df,3pd)//MP2/6-311G(2d,2p) and the recommended activation energies is reasonably good, with errors that range from 0.2 to 6 kJ mol$^{-1}$. It is interesting to notice that the errors obtained at the lower level PMP4(SDTQ)/6-311G(3df,2p)//MP2/6-311G(2d,2p) range from 0.3 to 4.0 kJ mol$^{-1}$. These results are encouraging in view of the fact of the considerable savings in computational expense when using the lower level. The results depicted in Table 2 indicate that the VAB's increase with fluorine substitution while the corresponding heats of reaction decrease. The opposite trend is observed in the case of chlorine and bromine substitution.

**4. Kinetic Parameters.** Table 3 lists the Arrhenius *A* factor and $E_a/R$ values obtained from fitting of the rate constants computed over the temperature range 250−400 K. Table 3 also shows the rate constants at 298 K, computed at the PMP4(SDTQ)/6-311G(3df,2p)//MP2/6-311G(2d,2p) and PMP4(SDTQ)/6-311++G(3df,3pd)//MP2/6-311G(2d,2p) levels of theory. The experimental values recommended in the literature are shown in the same table. The ratios between the theoretical and the experimental rate constants at 298 K are also reported in Table 3. With the exception of the reaction of OH with trichloromethane ($CHCl_3$), a reasonable agreement is observed between the theoretical and experimental values. The *A* factors computed at both levels of theory are very close, and they are found to be within a factor of 1.0−2.5 of the values reported in the literature. It is interesting to notice that the values of $E_a/R$ computed with the smaller basis set are closer to the experimental values (maximum deviation = 15.6%, average deviation = 9.4%) when compared to the corresponding $E_a/R$'s computed with the larger basis sets (maximum deviation = 51.4%, average deviation = 19.4%). The same trends are observed in the case of the reaction rate constants, where better agreements with the experimental values are obtained when using the smaller basis sets (see Table 3). Even though not shown, it was found that the TST treatment of the 12 reactions under study, together with Wigner's tunneling correction, gives linear Arrhenius plots similar to the ones derived from experimental data over the same temperature range (250−400 K). Overall, these results are in good agreement with the findings reported in our previous paper[1] and suggest that PMP4(SDTQ)/6-311G(3df,2p)//MP2/6-311G(2d,2p) is a good compromise between accuracy and computational expense in the theoretical treatment of hydrogen abstraction reactions between OH radicals and halomethanes. Consequently, this seems to be the method of choice for computing rate constants within a factor of 2−3 with respect to the experimental values over the temperature range 250−400 K.

The case of the abstraction reaction OH + $CHCl_3$ requires special attention. Even though the kinetic parameters computed with the smaller basis sets are closer to the experimental values, larger deviations from the experimental values are observed compared to the results obtained for the other 11 reactions. This can be attributed to the fact that a relatively small activation barrier characterizes this reaction, and canonical transition state theory, TST, might not be entirely adequate. As indicated in Table 2, the activation energy is underestimated at both levels of theory used in this work. This amplifies the overestimation of the reaction rate constants by TST. This conclusion is confirmed by the fact that a significantly better agreement is obtained if the rate constant is computed without including tunneling corrections (see Table 3). In such cases, Variational transition state theory[17] and more sophisticated models for tunneling corrections such as the ones developed by Truhlar's[18] and Miller's groups[19] seem to be the methodologies of choice. The results shown in Table 2 clearly indicate that these problems are more significant in the case of the chlorinated methanes $CH_3Cl$, $CH_2Cl_2$, and $CHCl_3$, where the vibrationally adiabatic barriers are considerably low, in contrast to the corresponding values of their fluorinated counterparts ($CH_3F$, $CH_2F_2$, and $CHF_3$). In addition to these very important issues, it is also possible that the existence of the complex formed in the entrance channel (not discussed in this work) could affect the energetics and kinetics of the reaction. Moreover, the optimized structures obtained at MP2/6-311G(2d,2p) can be considerably different from the geometries of the corresponding stationary points (reactants, complexes, and transition states) in the PMP4(SDTQ) surfaces computed with the 6-311G(3df,2p) and 6-311++G(3df,3pd) basis sets. This could explain why a decrease in the barriers is observed when chlorine substitution increases, in contrast to the trend found in the case of the fluorinated species. However, careful examination of the hydrogen-atom abstraction reactions under study (results not shown) indicates that similar trends in the energetics are observed at the UMP2/6-311G(2d,2p) and PMP4/6-311G(3df,2p)//UMP2/6-311G(2d,2p) levels of

**TABLE 3: Summary of Kinetic Parameters Calculated at PMP4(SDTQ)/6-311G(3df,2p)//MP2/6-311G(2d,2p) and PMP4(SDTQ)/6-311++G(3df,3pd)//MP2/6-311G(2d,2p) Levels of Theory Including Wigner Tunneling Correction**

| | | $E_a/R$ (K) | $A$, $10^{-12}$ [a] | $k$(theory,298 K), $10^{-15}$ [a] | {$k$(theory)/ $k$(exptl)} (298 K) |
|---|---|---|---|---|---|
| OH + $CH_3F$ | PMP4(SDTQ)/6-311G(3df,2p) | 1585 | 1.9 | 9.3 | 0.5 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | 1340 | 1.9 | 21 | 1.1 |
| | literature[b] | 1500 | 3.0 | 20 | |
| OH + $CH_3Cl$ | PMP4(SDTQ)/6-311G(3df,2p) | 1500 | 5.7 | 37 | 1.0 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | 1015 | 5.7 | 189 | 5.3 |
| | literature[b] | 1400 | 4.0 | 36 | |
| OH + $CH_3Br$ | PMP4(SDTQ)/6-311G(3df,2p) | 1610 | 5.4 | 24 | 0.8 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | 1190 | 5.4 | 100 | 3.4 |
| | literature[b] | 1470 | 4.0 | 29 | |
| OH + $CH_2F_2$ | PMP4(SDTQ)/6-311G(3df,2p) | 1680 | 4.8 | 17 | 1.7 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | 1595 | 4.8 | 23 | 2.3 |
| | literature[b] | 1550 | 1.9 | 10 | |
| OH + $CH_2FCl$ | PMP4(SDTQ)/6-311G(3df,2p) | 1415 | 3.9 | 34 | 0.9 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | 1160 | 3.9 | 80 | 2.1 |
| | literature[b] | 1270 | 2.8 | 39 | |
| OH + $CH_2Cl_2$ | PMP4(SDTQ)/6-311G(3df,2p) | 905 | 2.4 | 115 | 1.0 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | 510 | 2.4 | 433 | 3.9 |
| | literature[b] | 1050 | 3.8 | 110 | |
| OH + $CH_2ClBr$ | PMP4(SDTQ)/6-311G(3df,2p) | 945 | 2.2 | 92 | 0.9 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | 590 | 2.2 | 304 | 3.0 |
| | literature[b] | 930 | 2.3 | 100 | |
| OH + $CH_2Br_2$ | PMP4(SDTQ)/6-311G(3df,2p) | 995 | 2.5 | 89 | 0.75 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | 690 | 2.5 | 247 | 2.1 |
| | literature[b] | 900 | 2.4 | 120 | |
| OH + $CHF_3$ | PMP4(SDTQ)/6-311G(3df,2p) | 2745 | 2.0 | 0.20 | 0.7 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | 2640 | 2.0 | 0.28 | 1.0 |
| | literature[b] | 2440 | 1.0 | 0.28 | |
| OH + $CHF_2Cl$ | PMP4(SDTQ)/6-311G(3df,2p) | 1740 | 1.6 | 4.7 | 1.0 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | 1540 | 1.6 | 9.1 | 1.9 |
| | literature[b] | 1600 | 1.0 | 4.7 | |
| OH + $CHF_2Br$ | PMP4(SDTQ)/6-311G(3df,2p) | 1505 | 1.5 | 10 | 1.0 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | 1375 | 1.5 | 15 | 1.5 |
| | literature[b] | 1400 | 1.1 | 10 | |
| OH + $CHFCl_2$ | PMP4(SDTQ)/6-311G(3df,2p) | 1055 | 1.5 | 44 | 1.7 |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | 765 | 1.5 | 115 | 4.4 |
| | literature[b] | 1250 | 1.7 | 26 | |
| OH + $CHCl_3$ | PMP4(SDTQ)/6-311G(3df,2p) | 345 (855) | 0.9 (0.9) | 283 (51) | 2.9 (0.5) |
| | PMP4(SDTQ)/6-311++G(3df,3pd) | 10 (515) | 0.9 (0.9) | 870 (160) | 8.9 (1.6) |
| | literature[b] | 900 | 2.0 | 98 | |

[a] Units are $cm^3 \cdot molecule^{-1} \cdot s^{-1}$. [b] Literature values are taken from ref 2 and ref 14 for the reaction OH + $CH_2ClBr$. Values in parentheses correspond to the kinetic parameters without tunneling correction.

theory. The decrease in the barrier height with chlorine substitution has also been observed by Rayez et al. in an ab initio study of the H-atom abstraction of a series of halomethanes by chlorine atoms.[20]

Regardless of these problems, the use of PMP4(SDTQ)/6-311G(3df,2p)//MP2/6-311G(2d,2p) in the case of OH + $CHCl_3$ provides a rate constant that is approximately 3 times the experimental value, which may be adequate for lifetime estimations suitable for use in screening environmental acceptability of proposed industrial compounds.

## Conclusions

In this study, we have confirmed our previous observation that calculations at the UMP2 level of theory with the 6-311G(2d,2p) basis set provide reliable values of the geometric parameters in the case of hydrogen-atom abstraction reactions of halomethanes by OH radicals. Calculated reaction enthalpies, as before, depend on the level of theory, but were all within 0.2−15 kJ $mol^{-1}$ when computed by direct subtraction of the energies between products and reactants, and 0.1−10 kJ $mol^{-1}$ when isodesmic corrections were applied. The calculated kinetics of the reactions, which depend strongly on the calculated energetics, also differed for the two levels of theory tested. Surprisingly, the calculations at the lower level of theory, the PMP4(SDTQ) method with a 6-311G(3df,2p) basis set, appear to produce kinetic results which are in better agreement with experiment as those derived from calculations at the more computationally intensive PMP4(SDTQ) method with the 6-311++G(3df,3pd) basis set. Indeed, for this limited reaction set the calculated activation energies appear to be somewhat better for the lower level of theory. It would appear that the lower level provides a fortuitous but systematic cancellation of errors (probably resulting from a balance between basis set size and perturbation theory) that leads to better kinetic parameters in the case of hydrogen-atom abstraction reactions between OH radicals and halomethanes. This is a quite encouraging result, since it suggests that this less computationally intensive approach may be adequate in the creation of a screening tool for the environmental acceptability of new chemical compounds.

It is important to point out that in this project we are not developing new theory; nor are we attempting to adjust the theory to fit experimental data. We are applying conventional theoretical methodologies in order to build a screening tool, which will allow the estimation of the reactivity of new molecules toward the hydroxyl radical, leading to the systematic estimation of the atmospheric effects of these molecules. Further refinements in theoretical methods leading to faster and accurate calculations should allow additional improvement in this tool.

In particular, better approximations which lead to the efficient calculation of accurate tunneling correction factors as well as the efficient use of variational transition state theory in reactions characterized by low barriers seems to be of critical importance.

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**Supporting Information Available:** Tables of (i) the optimized geometry parameters of the halomethanes, halomethyl radicals, and transition states (Tables1S−5S), (ii) their vibrational frequencies (Tables 6S−8S), and (iii) the literature enthalpy values used for the calculation of the "experimental" reaction enthalpy (Table 9S). This material is available free of charge via the Internet at http://pubs.acs.org.

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